

PATENT SPECIFICATION

(11) 1 579 159

159

- (21) Application No. 26800/77 (22) Filed 27 Jun. 1977
 (31) Convention Application No. 2628987 (32) Filed 28 Jun. 1976 in
 (33) Fed. Rep. of Germany (DE)
 (44) Complete Specification Published 12 Nov. 1980
 (51) INT. CL.³ C07C 29/14 31/02 //
 B01J 23/84
- (52) Index at Acceptance
 C2C 20Y 30Y 360 361 36Y 413 414 415
 507 509 50Y 568 569 623 65Y 66Y
 FB YK
 B1E 1168 1285 1315 1331 1441 1463
 1513 1514 1611 1701 AA



1 579

(54) MANUFACTURE OF ALKANOLS

5 (71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

10 The present invention relates to a process for the manufacture of an alkanol of 3 to 5 carbon atoms by hydrogenating the corresponding alkanal in the liquid phase in the presence of water, using a nickel-containing supported catalyst.

15 Apart from the embodiment according to the invention, numerous variants of this process are generally known and therefore only the principle requires explanation. In all cases, the aldehyde is hydrogenated at from 100 to 220°C and from 8 to 300 bars hydrogen pressure in the liquid phase over a catalyst. In order to counteract the formation of ethers, which is undesirable, the reaction is carried out in the presence of a little water, but this lowers the life of the catalyst. Nevertheless, other by-products are also formed during the hydrogenation, which make it necessary to distil the crude alcohol, even if pure aldehydes are used as the starting materials.

20 There have therefore been many attempts to overcome these disadvantages by modifying the process conditions and above all by modifying the hydrogenation catalyst. Hitherto, however, these attempts have not been successful.

25 The present invention seeks to improve the hydrogenation of alkanols of 3 to 5 carbon atoms so as to make it unnecessary to purify the alcohols by distillation and so

as to increase the life of the catalyst.

30 According to the invention there is provided a process for hydrogenating an alkanal of 3 to 5 carbon atoms to give the corresponding alkanol carried out at from 130 to 190°C and from 30 to 300 bars hydrogen pressure in the liquid phase in the presence of water using a nickel-containing supported catalyst, wherein the active mass of the catalyst used comprises from 40 to 80% by weight of nickel, from 10 to 50% by weight of copper and from 2 to 10% by weight of manganese.

35 Suitable carriers for the catalyst include are the customary materials, e.g. silicic acid, silicates and aluminum oxide. Depending on the size of the particles, the mean diameter of which is preferably from 4 to 8 mm, this material absorbs, when the catalyst is prepared in accordance with a conventional technique, an amount of the active metals corresponding to from 15 to 35% of the total mass of the catalyst.

40 The catalysts to be used according to the invention may be manufactured, for example, by impregnating the carrier with an aqueous solution of Ni nitrate, Cu nitrate and Mn nitrate, containing the metals in proportion to achieve the above percentages in the active mass, then drying the particles and repeating this process until the desired amount of metal has been applied to the carrier. The material is then heated, e.g. in air at from about 500 to 600°C, to convert the metal salts to the corresponding oxides. Before being used for the hydrogenation reaction, the oxides are then reduced to the active metal form, e.g. at from 280 to 300°C. The reduction can be carried out in the hydrogenation reactor but in general it is

45

50

55

60

65

70

75

80

- more economical to use a separate apparatus for the reduction. The amount of catalyst is preferably such that during the hydrogenating from 40 to 100 g of active metal are available per mole of alkanal, assuming a residence time of one hour. 70
 The hydrogenation itself is carried out under the stated conditions. Conventional, preferably continuous, methods may be used. To facilitate heat transfer it is advisable to dilute the alkanal, preferably with the product of the reaction, i.e. with the corresponding alkanol. As a rule, from 4 to 8 l of the alkanol are used for this purpose per 1 of alkanal. To repress the formation of ethers it is furthermore advantageous if the reaction is carried out in the presence of from 50 to 200 ml of water per 1 of alkanal. After completion of the reaction, the water can be removed from the alkanol, with little expenditure of energy, by azeotropic distillation, and can be recycled, with the alkanol passing over at the same time, to the hydrogenation stage. 80
 The process according to the invention is of the greatest commercial importance for the manufacture of alkanols via the hydroformylation of olefins of 2 to 4 carbon atoms (i.e. by the oxo synthesis). For example, if propylene is hydroformylated using a cobalt catalyst, a crude mixture of about 60% by weight of n-butyraldehyde, 20% by weight of iso-butyraldehyde and 12% by weight of butanols, with a few by-products, is obtained. The hydrogenation of this crude mixture (after removing the hydroformylation catalyst) is disadvantageous because n-butanol and iso-butanol are separated much less successfully by distillation than are the corresponding lower-boiling aldehydes. It is therefore evidently desirable first to obtain the alkanols in the pure form from the crude mixture and then to carry out the hydrogenation. Hitherto, however, this approach offered no advantages since the alkanols had to be subjected to yet a further total distillation. Similar considerations apply to the manufacture of propan-1-ol and of the pentanols obtainable by hydroformylation. 90
 The present process for the first time makes it unnecessary to carry out a further purification of the alkanols, at least for most industrial purposes. The amount of high-boiling residue is below the limit of detection and the carbonyl number and acid number are less than 0.1. Contrary to expectations, the catalyst to be used according to the invention furthermore has twice the lift of the conventional supported catalysts with nickel and molybdenum as active components. 100
Example 1
 Per hour, 5 tonnes of iso-butyraldehyde were hydrogenated, at from 155 to 185°C and 270 bars hydrogen pressure, in a large industrial hydrogenation unit consisting of two high pressure reactors (connected in series), each of 6 m³ capacity and filled in total with 11 tonnes of catalyst. A volume ratio of aldehyde to alcohol of 1:6 was maintained in the reactors by recycling the iso-butanol. 110
 The iso-butyraldehyde was produced by hydroformylation of propylene. After isolation from the crude mixture, it contained virtually no impurities, but 70 ml of water per liter were added before the hydrogenation. 120
 The catalyst support (carrier) consisted of silicic acid of mean particle diameter 6 mm. In the active, reduced form it contained a total of 25% by weight of metal, which in turn was composed of 70% by weight of Ni, 25% by weight of Cu and 5% by weight of Mn, making a total of 100%. The catalyst was produced in the conventional manner by repeated impregnation, with intermediate drying, of the carrier, the impregnation being carried out with an aqueous solution containing Ni nitrate, Cu nitrate and Mn nitrate, and the salts being converted to the oxides. The active form was produced prior to the hydrogenation in the hydrogenation reactor. 130
 The aqueous crude iso-butanol was 99.5% pure (leaving water out of account). The by-products it contained were (by weight) 0.14% by weight of di-iso-butyl ether, 0.16% of propanol, 0.09% of n-butanol and 0.11% of other materials. High-boiling constituents were not detectable and the carbonyl number and acid number were less than 0.1. After removing water by azeotropic distillation, the iso-butanol was 99.9% pure.
 Over a period of observation of 18 months, it was unnecessary to regenerate the catalyst, and no decrease in catalyst activity was detected.
- Example 2**
 n-Butyraldehyde was hydrogenated to n-butanol under the conditions of Example 1, but in an experimental apparatus at 160°C and 40 bars hydrogen pressure. 115
 The butanol obtained was 98.8% pure. The by-products detected were 0.9% by weight of di-n-butyl ether and 0.3% by weight of high-boiling constituents. The acid number and carbonyl number were less than 0.1.
- Example 3**
 Propionaldehyde was hydrogenated to propanol under the conditions of Example 1, but in an experimental apparatus and at 150°C and 270 bars hydrogen pressure. The propanol obtained was 99.7% pure. The

by-products detected were 0.01% by weight of pentanol, 0.07% by weight of propionaldehyde dipropylacetal and 0.02% by weight of 2-methyl-pentanol. The acid number was 5 0.25 and the carbonyl number 0.03.

WHAT WE CLAIM IS:-

- 10 1. A process for hydrogenating an alkanal of 3 to 5 carbon atoms to give the corresponding alkanol, carried out at from 130 to 190°C and from 30 to 300 bars hydrogen pressure in the liquid phase in the presence of water using a nickel-containing supported catalyst, wherein the active mass of the catalyst used comprises from 40 to 15 80% by weight of nickel, from 10 to 50% by weight of copper and 2 to 10% by weight of manganese.
- 20 2. A process as claimed in claim 1, wherein the active mass of the catalyst comprises from 15 to 35% by weight of the total mass and is supported on silicic acid, a silicate or alumina.
- 25 3. A process as claimed in claim 1 or 2, wherein the alkanol starting material is diluted with from 4 to 8 liters of the alkanol product per liter of alkanal.
- 30 4. A process as claimed in any of claims 1 to 3, wherein the alkanal is reacted in the presence of from 50 to 200 ml of water per liter of alkanal.
- 35 5. A process as claimed in any of claims 1 to 4, wherein the alkanal starting material has been obtained in the hydroformylation of an olefin of 2 to 4 carbon atoms by the oxo synthesis followed by purification of the alkanal produced.
- 40 6. A process for the manufacture of an alkanol of 3 to 5 carbon atoms carried out substantially as described in any of the foregoing Examples.
- 45 7. Alkanols of 3 to 5 carbon atoms when manufactured by a process as claimed in any of claims 1 to 6.

45 J.Y. & G.W. JOHNSON,
Furnival House,
14-18 High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
50 Agents for the Applicants.